ENGINEERING CHANGE NOTICE

1. ECN 653809

Proj. ECN

2. ECN Category (mark one)	3. Originator's Name, Organization, MSIN, and Telephone No.	4. USQ Required?	5. Date
Supplemental [] Direct Revision [X] Change ECN [] Temporary [] Standby [] Supersedure [] Cancel/Void []	Duc M. Nguyen, Data Assessment and Interpretation, R2-12, 372-3042	[] Yes [X] No	05/26/99
	6. Project Title/No./Work Order No.	7. Bldg./Sys./Fac. No.	8. Approval Designator
	Tank 241-C-204	241-C-204	N/A
	9. Document Numbers Changed by this ECN (includes sheet no. and rev.)	10. Related ECN No(s).	11. Related PO No.
	WHC-SD-WM-ER-479, Rev. 0-B	ECNs: 612290, 644563	N/A

12a. Modification Work	12b. Work Package No.	12c. Modification Work Complete	12d. Restored to Original Condition (Temp. or Standby ECN only)
[] Yes (fill out Blk. 12b) [X] No (NA Blks. 12b, 12c, 12d)	N/A	N/A Design Authority/Cog. Engineer Signature & Date	N/A Design Authority/Cog. Engineer Signature & Date

13a. Description of Change 13b. Design Baseline Document? [] Yes [X] No

This ECN has been generated in order to update the document to reflect results of recent data/information evaluation.

Replace pages:

ES-1, ES-2, 5-1through 5-6, 6-1, 6-2, 7-3, and 7-4

14a. Justification (mark one)

Criteria Change	[X]	Design Improvement	[]	Environmental	[]	Facility Deactivation	[]
As-Found	[]	Facilitate Const	[]	Const. Error/Omission	[]	Design Error/Omission	[]

14b. Justification Details

A tank characterization report page change revision is required to reflect the results of recent evaluation of data/information pertaining to adequacy of tank sampling for safety screening purposes (Reynolds et al. 1999, Evaluation of Tank Data for Safety Screening, HNF-4217, Rev. 0, Lockheed Martin Hanford Corporation, Richland, Washington).

15. Distribution (include name, MSIN, and no. of copies)

See attached distribution.

RELEASE STAMP

DATE: JUN 07 1999

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16. Design Verification Required	17. Cost Impact				18. Schedule Impact (days)	
	ENGINEERING		CONSTRUCTION			
[ ] Yes	Additional	[ ] $	Additional	[ ] $	Improvement	[ ]
[X] No	Savings	[ ] $	Savings	[ ] $	Delay	[ ]

19. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 13. Enter the affected document number in Block 20.

SDD/DD	[ ]	Seismic/Stress Analysis	[ ]	Tank Calibration Manual	[ ]
Functional Design Criteria	[ ]	Stress/Design Report	[ ]	Health Physics Procedure	[ ]
Operating Specification	[ ]	Interface Control Drawing	[ ]	Spares Multiple Unit Listing	[ ]
Criticality Specification	[ ]	Calibration Procedure	[ ]	Test Procedures/Specification	[ ]
Conceptual Design Report	[ ]	Installation Procedure	[ ]	Component Index	[ ]
Equipment Spec.	[ ]	Maintenance Procedure	[ ]	ASME Coded Item	[ ]
Const. Spec.	[ ]	Engineering Procedure	[ ]	Human Factor Consideration	[ ]
Procurement Spec.	[ ]	Operating Instruction	[ ]	Computer Software	[ ]
Vendor Information	[ ]	Operating Procedure	[ ]	Electric Circuit Schedule	[ ]
OM Manual	[ ]	Operational Safety Requirement	[ ]	ICRS Procedure	[ ]
FSAR/SAR	[ ]	IEFD Drawing	[ ]	Process Control Manual/Plan	[ ]
Safety Equipment List	[ ]	Cell Arrangement Drawing	[ ]	Process Flow Chart	[ ]
Radiation Work Permit	[ ]	Essential Material Specification	[ ]	Purchase Requisition	[ ]
Environmental Impact Statement	[ ]	Fac. Proc. Samp. Schedule	[ ]	Tickler File	[ ]
Environmental Report	[ ]	Inspection Plan	[ ]		[ ]
Environmental Permit	[ ]	Inventory Adjustment Request	[ ]		[ ]

20. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing organization has been notified of other affected documents listed below.

Document Number/Revision	Document Number/Revision	Document Number Revision
N/A		

21. Approvals

	Signature	Date		Signature	Date
Design Authority			Design Agent		
Cog. Eng. D.M. Nguyen	Duc M. Nguyen	6/4/99	PE		
Cog. Mgr. K.M. Hall	[signature]	6/14/99	QA		
QA			Safety		
Safety			Design		
Environ.			Environ.		
Other			Other		
			DEPARTMENT OF ENERGY		
			Signature or a Control Number that tracks the Approval Signature		
			ADDITIONAL		

S

Tank Characterization Report for Single-Shell Tank 241-C-204

Duc M. Nguyen
Lockheed Martin Hanford Corp., Richland, WA 99352
U.S. Department of Energy Contract 8023764-9-K001

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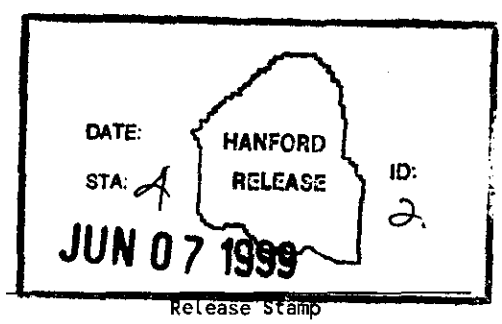
Abstract: N/A



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RECORD OF REVISION	(1) Document Number WHC-SD-WM-ER-479	Page 1

(2) Title
Tank Characterization Report for Single-Shell Tank 241-C-204

CHANGE CONTROL RECORD

(3) Revision	(4) Description of Change - Replace, Add, and Delete Pages	Authorized for Release	
		(5) Cog. Engr.	(6) Cog. Mgr. Date
0	(7) Initially released 9/12/96 on EDT 617542.	J. M. Conner	J. G. Kristofzski
0A RS	Incorporate per ECN-612290.	M. J. Kupfer 8-11-97	K. M. Hodgson 8-12-97
0B RS	Incorporate per ECN-644563.	M.J. Kupfer 9-14-98	K.M. Hodgson 9-16-98
0-C RS	Incorporate per ECN-653809.	D.M. Nguyen 6/4/99	K.M. Hall 6/4/99

EXECUTIVE SUMMARY

This tank characterization report summarizes the information on the historical uses, present status, and the sampling and analysis results of waste stored in single-shell underground storage tank 241-C-204 at the Hanford Site. This report supports the requirements of *Hanford Federal Facility Agreement and Consent Order*, Milestone M-44-09 (Ecology et al. 1996). Analytical results indicate the tank may pose a safety concern based on the decision limits of the *Tank Safety Screening Data Quality Objective* (Dukelow et al. 1995). Although tank samples exhibit energetics potential and total organic carbon (TOC) in excess of the limits in the data quality objective (DQO), the tank contains sufficient moisture to mitigate an exothermic event. Adiabatic calorimetry results indicate the waste will not propagate a reaction. Therefore, no imminent safety concern exists.

Tank 241-C-204 is one of 16 single-shell underground waste storage tanks located in the C Tank Farm in the 200 East Area of the Hanford Site. The maximum capacity of tank 241-C-204 is 210 kL (55 kgal). The tank was filled with waste in January, 1948. Supernatant liquor was pumped from the tank in 1953, and water was added. The metal waste was removed for uranium recovery in early 1955, and the tank began receiving strontium semiworks waste late that same year. The tank received transfers of waste from the Hot Semiworks Plant in May 1956 and in the fourth quarter of 1967. Supernate was pumped from the tank in 1970 and 1977 leaving an 11 kL (3 kgal) heel of solids. Because the Hot Semiworks Plant was operated as a pilot plant for separations processes, it is difficult to estimate the contents of the tank based on process history. Estimates generated prior to

sampling assumed the remaining tank waste was metal waste. Based on sampling results, it is believed that little metal waste remains in the tank.

A description and status of the tank are summarized in Table ES-1. The tank currently contains 11 kL (3 kgal) of waste in the form of sludge. The latest tank photographs (1986) show a mixed yellow and brown, wet surface with crust near the walls. When the 1988 photographs are compared with earlier ones (1977, 1980, and 1983), it is evident the tank contents are slowly drying out. Temperature data, available for 1975 to 1978, indicate the tank temperature remained below 21 °C (70 °F) during this period. Although thermocouple elevations are not known, it is assumed that thermocouples were in the waste prior to tank liquids being pumped in 1977. The current waste level is approximately 0.4 m (1.3 ft).

This report describes data from the May 1995 auger sampling event. Auger samples 95-AUG-022 and 95-AUG-023 were taken and analyzed according to the requirements of the safety screening DQO. Energetics, moisture, and total alpha content were determined. Secondary analyses were performed to determine the TOC content and to test for energetic potential under adiabatic conditions. In addition, one sample was analyzed for organic compounds at the request of the Organic Safety Program. Data from the June 1996 tank headspace flammability screening data are reported as well.

5.0 INTERPRETATION OF CHARACTERIZATION RESULTS

This section evaluates the overall quality and consistency of the available results for tank 241-C-204, and it assesses and compares the results against historical information and program requirements. The assessment of the tank profile is limited because of the small data set required for safety screening and problems with sample recovery.

5.1 ASSESSMENT OF SAMPLING AND ANALYTICAL RESULTS

This section evaluates sampling and analysis factors that may impact data interpretation. These factors are used to assess the quality and consistency of data and to identify any limitations in the data use.

Because of the small number of analyses conducted on tank 241-C-204 auger samples and the problems encountered in sampling, information is limited. The intent of the sampling event was to screen the tank for safety issues. A safety issue was identified (exothermic potential), and secondary analyses were conducted. No statements regarding the homogeneity of tank contents can be inferred as both samples were recovered from the same tank access point (riser 7) and were contaminated with rag material. Nevertheless, the information was useful, and some qualified statements regarding tank contents can be made. Results indicate that an exothermic event is not possible, because of the sluggish reaction of the waste and high moisture content.

5.1.1 Field/Laboratory Observations

Both augers encountered a rag in the tank. For auger sample 95-AUG-022, field personnel reported hitting a very hard layer near the projected tank bottom. Because depth measurements are not always exact, the sampling crew concluded that the tank bottom may have been reached. Augering was stopped, and the sample was extracted. For auger sample 95-AUG-023, a similar hard layer was encountered four inches higher than the previous sample. In retrospect, the tank bottom may not have been reached on either sample, and augering may have been hindered because the rag was bound up in the auger. Nevertheless, sufficient tank waste material was recovered to perform safety screening analyses according to the SAP (Schreiber 1995).

Extrusion of both augers was difficult because of the rag which was jammed between the auger and the auger sleeve. The rag caught by both augers is visible in in-tank photographs (see Figure 5-1). Upon extrusion, hot cell technicians were directed to segregate the rag material from the tank waste material. No rag fibers were visible in the segregated tank waste. Subsequently, hot cell chemists reported seeing rag fibers in the sample air-dried in preparation for adiabatic calorimetry. Even after several weeks of drying, the sample

appeared wet and had a gummy consistency, perhaps indicating a high organic content. Visible fibers were removed before the analysis.

No other chemist reported seeing rag fibers. This is significant because in the other analyses, the subsamples are quite small (approximately 25 mg for DSC and TGA runs and 0.5 g to 1.0 g for a TOC analysis or fusion). For these small sample sizes, the absence of visible fibers does not rule out the possibility of contamination (on the rag material or the material itself), but it does indicate that large exotherms and high TOC results are largely attributable to organics in the tank waste. However, contamination from the rag material cannot be ruled out.

The conclusion from adiabatic calorimetry is that the sample would not support a propagating combustion reaction. This result, coupled with the high moisture content of the samples (55 percent), rules out any imminent concern.

5.1.2 Quality Control Assessment

The usual quality control assessment includes an evaluation of the appropriate standard recoveries, matrix spike recoveries, duplicate analyses, and blanks that are performed in conjunction with the chemical analyses. All the pertinent quality control tests were conducted on the 1995 auger samples, allowing a full assessment regarding the accuracy and precision of the data. The specific criteria for all quality control checks were given in the SAP (Schreiber 1995, Conner 1996a). Quality control results outside these criteria were identified in the data summary tables (see Section 4.0).

The standard and matrix spike recovery results provide an estimate of the accuracy of the analysis. If a standard or spike recovery is above or below the given criterion, the analytical results may be biased high or low, respectively. All standard recoveries were within the defined criterion. The single matrix spike recovery for total alpha activity was below the 90 to 110 percent criterion (61.9 percent recovery). This may have been caused by low sample activities and self-shielding. The single matrix spike recoveries for TIC and TOC were also outside the criterion.

Analytical precision is estimated by the relative percent difference (RPD), which is defined as the absolute value of the difference between the primary and duplicate samples, divided by their mean, times one hundred. The SAP criterion for analytical precision is $\leq$ 10 percent for all analytes. Total alpha activity had two of three RPDs outside this limit. Considering that no result was more than 10 times the detection limit, some variability is expected. Because all results were below the decision threshold of 41 μCi/g by a factor of 800 or more, reruns were not considered necessary (Conner 1995a). One of three TGA samples had an RPD above the $\leq$ 10 percent SAP limit. Both the TIC and TOC RPDs were above the criterion as well as the single DSC sample for which an RPD was calculable. The high RPD result for the DSC analyses was probably caused by the unusual exothermic behavior and the small sample size. The poor reproducibility of DSC and TOC results may have been

caused by the extraordinarily high organic content or contamination by a rag that was extruded with the samples (leading to poor homogenization).

5.1.3 Data Consistency Checks

Comparing different analytical methods is helpful when assessing data consistency and quality. Because of the limited data, few such checks can be made. The only comparison provided here is to compare the organic carbon results from the Westinghouse Hanford Company and the Pacific Northwest National Laboratory with the organic speciation results from the Pacific Northwest National Laboratory.

The TOC results of approximately 13 percent, which were generated at the 222-S laboratory, are over twice the TOC value of six percent which was generated by the PNNL. This discrepancy may be due to sample inhomogeneity or differences in the analytical procedures. The tributyl phosphate results of 33 percent (equivalent to 18 percent TOC) determined by gas chromatography/mass spectrometry are well above either reported TOC value. However, Mong and Campbell (Conner 1996b) note that the persulfate oxidation method used to generate the TOC data does not give complete nor quantitative results for tributyl phosphate. Therefore, the TBP results are not inconsistent with the lower TOC results.

5.2 COMPARISON OF HISTORICAL AND RECENT ANALYTICAL RESULTS

Because the 1972 and 1975 samples were liquids and the tank now contains only solids, no extensive comparison of results is attempted. It is interesting to note that exotherms were detected in the 1972 sample and in the 1995 augers, but they were not detected in the dilute 1975 sample.

5.3 COMPARISON OF ANALYTICAL AND TRANSFER DATA

The HTCE predictions for the contents of tank 241-C-204, taken from *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 3* (Agnew et al. 1996), are shown in Table 5-1 with the analytical results from the 1995 auger sampling event. Because the HTCE values have not been validated, the comparison is for information only.

Comparisons were possible for only four analytes. The total inorganic carbon comparison demonstrated the best agreement. The water content predictions agreed moderately, but there was poor agreement between the two data sets for total alpha activity and extremely poor agreement for total organic carbon. Reasons for the discrepancies could include the following: high variability in the waste stream modeled, incorrect modeling assumptions, or sampling complications such as the rag.

Table 5-1. Comparison of HTCE Predictions with the 1995 Analytical Results.

Analyte	HTCE Estimate[1]	1995 Analytical Result[2]	Relative Percent Difference
Total alpha activity	0.00263 μCi/g[3]	0.0322 μCi/g	170%
TOC	4,120 μg C/g	1.26E+05 μg C/g	Not applicable
TIC	9,180 μg C/g	10,500 μg C/g	13.4%
Water	44.1 wt.%	56.94 wt.%	25.4%

Notes:

[1]Agnew et al. (1996)
[2]Conner (1996b)
[3]The result is based only on a plutonium estimate.

5.4 EVALUATION OF PROGRAM REQUIREMENTS

The two auger samples taken from tank 241-C-204 in 1995 were acquired to meet the requirements of the original release of the safety screening DQO (Babad and Redus 1994). The headspace flammability screening conducted in 1996 was performed to satisfy a later version of the DQO (Dukelow et al. 1995). A vapor sample was taken in June 1996 to comply with the requirements of (Osborne et al. 1995). As analyses are not yet completed, these results will be addressed in a revision to this tank characterization report. Only safety screening issues are addressed at this time.

Data criteria in the original safety screening DQO (Babad and Redus 1994) are used to assess waste safety and to check for unidentified safety issues. The safety screening DQO indicates that two widely spaced vertical core samples would be a near optimum sampling scheme. The SAP (Schreiber 1995 and Conner 1996a) stated that although a second riser could be used with considerable effort, only one 12-in. riser was readily available for sampling. The SAP says "Discussions with personnel in the tank waste remediation system indicated that since samples out of both risers offered a separation of only two feet, in this case it was acceptable to take two samples out of the same riser, offering a separation of approximately 10 inches." It is worth noting that tank 241-C-204 is only 6.1 m (20 ft) in diameter, not 22.9 m (75 ft) in diameter as are most other waste tanks. Both augers hit a rag on the surface of the waste and may not have retrieved full length samples. However, sampling and analytical results of the collected sample material are considered sufficient to address the data needs specified in the safety screening DQO. Basis for the determination that the data needs have been sufficiently addressed is provided in Reynolds et al. (1999).

The analytical requirements of the DQO were to evaluate energetic potential by DSC and TGA and to evaluate the criticality potential by total alpha counting (see Table 5-2). All samples submitted for DSC exceeded the -481 J/g action limit. This triggered secondary

analyses consisting of TOC on two of three subsamples (one sample was completely used up during primary analyses) and adiabatic calorimetry on one of two archive samples. The TOC results were far over the action limit of 30,000 μg/g.

The SAP called for cyanide analyses once a sample exceeded the safety screening limit for energetics by DSC. However, cyanide analyses were not run for samples from tank 241-C-204 even though the safety screening limits for energetics were exceeded. Safety program personnel directed that the limited archive material be saved for more appropriate secondary analyses. Once the exothermic nature of the tank 241-C-204 auger samples was detected by DSC analyses, the transfer history of the tank was reviewed to identify the responsible waste stream. Transfers from the hot semiworks process (DeLorenzo et al. 1994) are suspected to be the source of the organics-rich waste found in tank 241-C-204. These waste streams and other streams directed to the tank do not contain ferrocyanide, the cyanide parent chemical of concern to the safety program. Therefore, analyzing tank 241-C-204 samples for cyanide was determined to be of little value.

The flammability issue of the DQO was met by combustible gas monitoring. Results indicate no flammability concern exists (0 percent of LFL).

The analytical requirements of the DQO were met. Although the DSC and TOC action limits were exceeded, the moisture content of 55 percent is well above the 20 percent level necessary for mitigation of an exothermic event (Dukelow et al. 1995). In addition, the results of adiabatic calorimetry indicate that the sample will not propagate a reaction. None of the analytical data indicate that the tank is unsafe according to the criteria in the DQOs (Babad and Redus 1994 and Dukelow et al. 1995).

Table 5-2. Comparison of 1995 Auger Sample Data to Safety Screening DQO Decision Criteria.

Decision Variable	Decision Criteria Threshold (Action Limit)	Number of Subsamples Outside Threshold/Total Subsamples
Total fuel content	> 481 J/g	3/3
Percent water	< 17 weight percent	0/3
Total alpha	> 41 μCi/g[1]	0/3
TOC	> 30,000 μg/g	2/2
Combustible gas meter	< 10 percent of LFL	0/1

Note:

[1]Derived from a specification of 1 g/L, assuming a waste density of 1.5 g/cm^3.

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6.0 CONCLUSIONS AND RECOMMENDATIONS

The waste in tank 241-C-204 was auger sampled in May, 1995, and the tank headspace was screened for flammable gases in June, 1996. The *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994 and Dukelow et al, 1995) governed the sampling and analysis of samples 95-AUG-022 and 95-AUG-023 and the flammability screening event.

Full vertical profiles of the tank waste probably were not obtained because the augers encountered a rag in the tank. However, analytical results of the collected samples are considered sufficient to address the data needs specified in the DQO (Reynolds et al. 1999). The analytical results on the retrieved waste indicate unexpectedly high energetics and TOC. Exotherms in excess of -1,234 J/g (dry basis) were detected (final values could not be obtained because the exotherms were still progressing at the temperature limit of the test, that is, 500 or 600 °C). The action limit was -481 J/g. The TOC results were approximately 13 percent (26 percent dry basis). Results of organic speciation suggest that the organic component is almost exclusively tributyl phosphate. The moisture content of the samples was 57 percent by TGA, and the total alpha concentration averaged 0.0322 μCi/g, well below the action limit of 41 μCi/g.

Although the DSC results exceeded the safety action limit, TGA results indicate the tank has sufficient moisture to mitigate any exothermic event. Further, the adiabatic calorimetry results indicate the sample will not propagate an exothermic reaction.

Headspace flammability is not a concern because the results of combustible gas monitoring indicate headspace gases are at 0 percent of the LFL.

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Project Title/Work Order		EDT No. N/A
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